

### Claims

1. A method of etching silicon nitride from at least one substrate comprising:

providing a closed-loop circulation system having a process chamber and a recirculation line fluidly coupled to the process chamber;

supplying sulfuric acid, phosphoric acid, and water to the closed-loop circulation system in predetermined amounts so as to form a mixture having a predetermined concentration ratio and a predetermined volume, the mixture filling the process chamber and overflowing into the recirculation line;

submerging at least one substrate in the mixture within the process chamber;

circulating the mixture through the closed-loop circulation system;

continuously measuring concentration ratio of the mixture with a concentration sensor;

comparing the measured concentration ratio to the predetermined concentration value to determine whether the measured concentration value is within a predetermined range of the predetermined concentration ratio; and

upon determining that the measured concentration ratio is not within the predetermined range of the predetermined concentration ratio, automatically feeding a volume of sulfuric acid, phosphoric acid, and/or water into the closed-loop circulation system while bleeding a substantially equal volume of the mixture from the closed-loop circulation system that will return the concentration ratio of the mixture back within the predetermined range during processing of the at least one substrate.

2. The method of claim 1 wherein the sulfuric acid, phosphoric acid, and water are initially supplied to the process chamber via dispense lines.

3. The method of claim 1 wherein the volume of sulfuric acid, phosphoric acid, and/or water added to the mixture during the feeding step are supplied via spike lines.

4. The method of claim 1 further comprising heating the mixture prior to submerging the at least one wafer therein.
5. The method of claim 4 wherein the mixture is heated to a temperature at or near 160-180°C.
6. The method of claim 5 wherein the mixture is heated to a temperature at or near 165°C.
7. The method of claim 1 wherein the predetermined concentration ratio is approximately 2 parts sulfuric acid, 2 parts phosphoric acid, and 1 part water.
8. The method of claim 1 further comprising filtering the overflowed mixture.
9. The method of claim 1 further comprising:

continuously measuring particle counts in the mixture with a particle counter;

comparing the measured particle count to a predetermined particle count to determine whether the measured particle count is greater than the predetermined particle count; and

upon detecting the mixture having a particle count that is greater than the predetermined particle count, automatically bleeding a volume of the mixture from the closed-loop circulation system and feeding a substantially equal volume of sulfuric acid, phosphoric acid, and/or water into the closed-loop circulation system that will return the particle count of the mixture back to or below the predetermined particle count during processing of the at least one substrate.

10. A method of etching silicon nitride from at least one substrate comprising:

(a) supplying sulfuric acid, phosphoric acid, and water to a process chamber in predetermined amounts so as to form a predetermined volume of mixture having a predetermined concentration ratio;

(b) circulating the mixture through the process chamber in a closed-loop circulation system;

(c) submerging at least one substrate in the mixture within the process chamber;

(d) bleeding a volume of mixture from the closed loop system so as to reduce the effect of etch-by-products in the circulating mixture; and

(e) feeding phosphoric acid, sulfuric acid, and/or water to replace the volume of mixture bled from the closed loop;

wherein the volume bled is selected to maintain or return the concentration ratio of the mixture to within a predetermined range of the predetermined concentration ratio.

11. The method of claim 10 wherein the bleeding and feeding of steps (d) and (e) are performed continuously or at set intervals.

12. The method of claim 10 further comprising:

(f) continuously measuring the concentration ratio of the mixture with a concentration sensor during processing of the at least one substrate;

(g) comparing the measured concentration ratio to the predetermined concentration value to determine whether the measured concentration value is within a predetermined range of the predetermined concentration ratio; and

(h) upon determining that the measured concentration ratio is not within the predetermined range of the predetermined concentration ratio, automatically performing steps (d) and (e).

13. A system for etching silicon nitride from at least one substrate comprising:

a closed-loop circulation system having a process chamber and a recirculation line fluidly coupled to the process chamber;

means for supplying sulfuric acid, phosphoric acid, and water to the closed-loop circulation system so as to form a predetermined volume of mixture having a predetermined concentration ratio;

means for flowing the mixture through the closed-loop circulation system;

a concentration sensor that continuously measures the concentration ratio of the mixture and produces a signal indicative of the measured concentration ratio during processing of at least one substrate in the process chamber;

means for feeding sulfuric acid, phosphoric acid, and water to the closed-loop circulation system;

means for bleeding the mixture from the closed-loop circulation system; and

a processor operably coupled to the concentration sensor, the feeding means, and the bleeding means;

wherein the processor is programmed so that upon receiving a signal indicative of a concentration ratio that is not within a predetermined range of the predetermined concentration ratio from the concentration sensor, the processor automatically activates the feeding means to add a volume of sulfuric acid, phosphoric acid, and/or water to the closed-loop circulation system and activates the bleeding means to drain a substantially equal volume of the mixture from the closed-loop circulation system during the processing of the at least one substrate that will return the concentration ratio of the mixture within the predetermined range of the predetermined concentration ratio.

14. The system of claim 13 wherein the process chamber is adapted to receive a plurality of substrates.

15. The system of claim 13 further comprising a filter operably coupled to the recirculation line.

16. The system of claim 13 further comprising a heater coupled to the recirculation line and adapted to heat the mixture.

17. The system of claim 13 wherein the means to supply sulfuric acid, phosphoric acid, and water to the process chamber are a plurality of dispense lines with valves.

18. The system of claim 17 wherein the means to feed sulfuric acid, phosphoric acid, and water to the mixture is a plurality of spike lines with valves.

19. The system of claim 13 wherein the means to supply sulfuric acid, phosphoric acid, and water to the process chamber and the means to feed sulfuric acid, phosphoric acid, and water to the mixture are the same.

20. The system of claim 13 wherein the means for bleeding comprises a bleed valve operably coupled to a bleed line.

21. The system of claim 13 further comprising:

a particle counter that continuously measures particle count of the mixture and produces a signal indicative of the measured particle count during processing of at least one substrate in the process chamber;

wherein the processor is also operably coupled to the particle counter; and

wherein the processor is further programmed so that upon receiving a signal indicative of a measured particle count above a predetermined particle count, the processor automatically activates the feeding means to add a volume of sulfuric acid, phosphoric acid, and/or water to the closed-loop circulation system and activates the bleeding means to drain a substantially equal volume of the mixture from the closed-loop circulation system during the processing of the at least one substrate that will return the particle count of the mixture back to or below the predetermined particle count.

22. A method of etching silicon nitride from at least one substrate comprising:

providing a closed-loop circulation system having a process chamber and a recirculation line fluidly coupled to the process chamber;

supplying a predetermined volume of an etchant to the closed-loop circulation system, the etchant filling the process chamber and overflowing into the recirculation line;

submerging at least one substrate in the etchant within the process chamber;

circulating the mixture through the closed-loop circulation system;

continuously measuring particle count of the etchant with a particle counter;

upon detecting the etchant having a measured particle count above a predetermined particle count, automatically bleeding a volume of contaminated etchant from the closed-loop circulation system while replacing the volume by feeding fresh etchant into the closed-loop circulation system during the processing of the at least one substrate that will return the particle count of the etchant within the closed-loop circulation system to or below the predetermined particle count.

23. A system for etching silicon nitride from at least one substrate comprising:

a closed-loop circulation system having a process chamber and a recirculation line fluidly coupled to the process chamber;

means for supplying a pre-determined volume of etchant to the closed-loop circulation system;

means for flowing the mixture through the closed-loop circulation system;

a particle counter that continuously measures particle count within the etchant and produces a signal indicative of the measured particle count during processing of at least one substrate in the process chamber;

means for feeding etchant to the closed-loop circulation system;

means for bleeding the etchant from the closed-loop circulation system; and

a processor operably coupled to the particle counter, the feeding means, and the bleeding means;

wherein the processor is programmed so that upon receiving a signal indicative of a measured particle count above a predetermined particle count, the processor automatically activates the feeding means to add a volume of fresh etchant to the closed-loop circulation system and activates the bleeding means to drain a substantially equal volume of the etchant from the closed-loop circulation system during the processing of the at least one substrate that will return the particle count of the mixture back to or below the predetermined particle count.